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Improved Silica Gel Cleanup Method for Organophosphorus Pesticides

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JOURNAL ARTICLE

IMPROVED SILICA GEL CLEANUP METHOD FOR ORGANOPHOSPHORUS PESTICIDES[1]

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ABSTRACT

Quantitative recovery of some organophosphorus pesticide residues has not been possible with existing silica gel-cleanup procedures. We have developed a modification that permits quantitative recovery of all organophosphorus pesticides tested except those with a carbamate functional group. The method uses a 3.5 g silica gel column with a 1% acetic acid wash to condition the column prior to the addition of the sample. Percentage recovery and standard deviation of compounds such as phorate and disulfoton are 96 (5.6) and 98 (1.0) respectively. Recoveries range from 92 to 101% for the 11 compounds tested.

INTRODUCTION

Silica gel microcolumns have been used for cleanup of sample extracts in the analysis of organophosphorus pesticide residues for many years(1-6); however, many of the organophosphorus pesticides currently on the market are difficult to recover from silica gel using existing elution patterns (6). Attempts to improve the recovery of fenthion during a field study led to the discovery that acetic acid conditioning of the silica gel improved the recovery dramatically(7). Lawrence and Leduc(8) also reported significant improvement in silica gel chromatography of organic acids and bases after the addition of small quantities of organic acids to the mobile phase.

After additional tests with other organophosphorus pesticides, we found that acetic acid conditioning improved the recovery of several organophosphorus pesticides that have been difficult to recover.

This paper describes a method that we believe will improve cleanup recovery of many organophosphorus pesticides. However, the work reported here does not constitute a thorough testing of this method with a large variety of substrates and pesticides.

EXPERIMENTAL SECTION

Apparatus. A Hewlett-Packard Model 5710 gas chromatograph (GC) equipped with nitrogen-phosphorus detectors and 182 cm x 2 mm i.d. glass columns packed with either 5% QF-1 on 80/100 mesh Gas Chrom Q or 0.75% OV-17/0.97% OV-210 on 100/120 mesh Supelcoport was used for analysis of all pesticides except temephos. Operating conditions were: oven temperature, 200°C (for all compounds except temephos and carbophenothion); injector temperature, 200°C; detector temperature, 300°C; helium carrier gas flowing at 30 mL/min. Detector gas flow rates were 4.0 mL/min hydrogen and 100 mL/min air. The chromatography of carbophenothion was carried out at 250°C oven temperature, and temephos was analyzed on a capillary GC with an electron capture-detector and a 15 m x 0.32 mm i.d. capillary column coated with 1 µm film thickness of DB-1 from J&W Scientific. For the analysis of temephos, the oven temperature was programmed from 275 to 320°C @ 4°mL/min, and the helium carrier gas was maintained at a constant pressure of 10 psi. Data were collected and qualitatively and quantitatively analyzed on a Hewlett-Packard 3357 lab automation computer.

Glass columns. 200 mm x 9 mm i.d. Chromaflex columns (Kontes Glass Co., Vineland, N.J.) were used for sample cleanup.

Reagents. All solvents were nanograde (Burdick and Jackson Laboratories) or equivalent. Silica gel (Baker cat.# 3405, 60-200 mesh) was stored at 130 C. Reagent grade acetic acid was used to make the 1% (v/v) acetic acid in hexane used for column conditioning and elution.

Standards. All standards were obtained from the U.S. EPA Pesticide Repository (Las Vegas, Nevada). Primary standards (1.0 mg/mL were prepared in p-xylene, working standards (0.040 to 0.10 ng/µL) were prepared in hexane.

Cleanup procedure. Silica gel, which had been stored at 130°C and mixed well to avoid settling of the fines, was deactivated by the addition of 20% (w/w) distilled water in and was tumbled on a roto rack for 2h prior to use. Cleanup columns were prepared by plugging with glass wool and adding 3.5 g silica gel, followed by 2.0 g of anhydrous sodium sulfate (granular). The columns were washed with 10 mL of 1.0% acetic acid in hexane before and after the sample introduction, and eluant was discarded. If the column is properly packed, the flow rate should be approximately 1 mL/min. Fraction I was eluted with 20 mL of 5% (v/v) ethyl ether in hexane. Fraction II was eluted with 20 mL of 10% (v/v) ethyl ether in hexane. The eluants were collected in 25 mL concentrator tubes (Kontes) and concentrated to not less than 1.0 mL with a gentle stream of nitrogen while heating in a 30°C water bath.

RESULTS AND DISCUSSION

Our method was tested with several organophosphorus pesticides; their elution patterns are shown in Table I. The recoveries of these pesticides were evaluated with solutions of the pesticides both in pure hexane and in hexane extracts of oyster tissue, and there was no significant difference. With the exception of those organophosphorus pesticides which have a carbamate functional group (such as phosphamidon), all organophosphates that have been checked by this method have had recoveries of at least 90%. This includes several pesticides that were reported to have recoveries of less than 60% (i.e., phorate and disulfoton). The average percentage recovery is shown in Table II. A comparison of the recoveries found by this method and the recoveries found by the method of Thompson et al. (6) is shown in Table III. This method has been tested on a large number of fenthion and temephos samples from field studies (7,9).

The reason for the improved recovery is not known. The increased stability of organophosphates in a mild acid may be a factor; however, another possibility is the localization of the acetic acid to active sites on the silica gel, preventing the organophosphorus pesticides from binding with these sites. The latter reason now seems more likely since we found that a variety of polar solvents (such as benzene and chloroform) used

in place of the acetic acid will also improve the recovery, but not as much as the acetic acid. This explanation is also consistent with Snyder's model of liquid-solid chromatography (10-11). In either case, the result is an improvement in the recovery that will probably be helpful with many of the organophosphates that are difficult to recover from cleanup columns.

Table I

Elution Pattern of Several Organophosphorus Pesticides on Silica Gel, Using 1% Acetic Acid Conditioning Wash.

Fraction I 5% ethyl ether in hexane	Fraction II 10% ethyl ether in hexane
Carbophenothion	DEF
Chlorpyrifos	Diazinon
Disulfoton	Malathion
Ethyl Parathion	Temephos
Fenthion	
Leptophos	
Phorate	

Table II

Average Percentage Recovery of Several Organophosphorus Pesticides, Using an Acetic Acid Conditioned Silica Gel.

Pesticide	N	Amt added	%recovery(sd)
Carbophenothion	7	0.1 µg	97 (3.2)
Chlorpyrifos	19	0.1 µg	97 (4.1)
DEF	13	0.1 µg	100 (4.0)
Diazinon	14	0.1 µg	92 (4.4)
Disulfoton	4	10.0 µg	98 (1.0)
Ethyl Parathion	14	0.1 µg	98 (4.2)
Fenthion	9	0.1 µg	101 (11.5)
Leptophos	7	0.1 µg	99 (1.5)
Malathion	11	0.1 µg	93 (3.5)
Phorate	18	0.1 µg	96 (5.9)
Temephos	7	1.0 µg	104 (8.2)

N = Number of determinations

Table III

Comparision of Percentage Recovery of Selected Organophosphorus Pesticides from Silica Gel Cleanup Columns

Compound	Thompson et al.	Lores et al.
Chlorpyrifos	87%	97%
DEF	90%	100%
Diazinon	104%	92%
Disulfoton	0%	98%
Ethyl Parathion	99%	98%
Fenthion	76%	98%
Leptophos	91%	99%
Malathion	78%	93%
Phorate	56%	96%

Literature cited

(1) Kadoum, A.M. Bull. Environ. Contam. Toxicol. 1967, 2, 264

(2) Kadoum, A.M. Bull. Environ. Contam. Toxicol. 1968, 2, 65

(3) Law, L.M.; Goerlitz, D.F. J. AOAC 1970, 53, 1276

(4) Leoni, V. J. Chromatog. 1971, 62, 63

(5) Sherma, J., Shafik; T.M. Arch. Environ. Contam. Toxicol. 1975, 3, 55

(6) Thompson, J.F.; Reid, S.J. Kantor, E.J. Arch. Environ. Contam. Toxicol. 1977, 6, 143

(7) Lores, E.M.; Moore, J.C.; Knight, J.; Forester, J.; Clark, J.; Moody, P. J. Chrom. Sci. 1985, 23, 124

(8) Lawrence, J.F.; Leduc, R. Anal. Chem. 1978, 50, 1161

(9) Lores, E.M.; Moore, J.C.; Moody, P.; Clark, J.; Forester, J.; Knight, J. Bull. Environ. Contam. Toxicol. 1985, 35, 308

(10) Snyder, L.R. Anal. Chem. 1974, 46, 1384

(11) Snyder, L.R.; Poppe, H. J. Chromatog. 1980, 184, 363

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